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(54) ANISOTROPICALLY ELECTROCONDUCTIVE ADHESIVE

(57)Abstract:

PURPOSE: To obtain an anisotropically electroconductive adhesive comprising an adhesive component having insulating properties and metal-containing particles dispersed into the adhesive component, bondable at a low temperature under low pressure in a short time, useful for electric connection between wiring boards having a wiring pattern on the surface of the boards.

CONSTITUTION: This adhesive comprises (A) an adhesive component having insulating properties, containing (i) an acrylic adherent component, (ii) a reactive component containing at least two (meth)acryloyl groups, (iii) a polymerization initiator and (B) a metal-containing particles (e.g. metal particles, insulation film coated metal particles obtained by coating the surface of metal particles with an insulating component, etc.) dispersed into the adhesive component, is cured by heating or by light irradiation and bonded to a material to be bonded. The component A comprises preferably 1-100 pts.wt. of the component (ii) based on 100 pts.wt. of the component (i) and 0.5-10 pts.wt. of the polymerization initiator based on 100 pts.wt. of the component (ii).

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Notes:

1. Untranslatable words are replaced with asterisks ("***").
2. Texts in the figures are not translated and shown as it is.

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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] Are the anisotropic conductive adhesives which consist of metal content grains distributed in the adhesives component which has insulation, and this adhesives component, and this adhesives component An acrylic adhesive property component, (Meta) Anisotropic conductive adhesives characterized by for this adhesives component hardening by heating or photoirradiation, and joining adherend by containing the reactant component which has at least two acrylyl groups, and a polymerization initiator.

[Claim 2] The above-mentioned adhesives component receives an acrylic adhesive property component and this acrylic adhesive property component 100 weight part. Anisotropic conductive adhesives given in the 1st clause of a claim characterized by containing the polymerization initiator of 0.5 - 10 weight part to the reactant component which has at least two acrylyl groups (meta) of a 1 - 100 weight part, and the reactant component 100 weight part which has these (meta) at least two acrylyl groups.

[Claim 3] Anisotropic conductive adhesives given in the 1st clause of a claim characterized by the above-mentioned polymerization initiator being a thermal polymerization initiator or a photopolymerization initiator.

[Claim 4] The acrylic ester 60 in which the above-mentioned acrylic adhesive property component has the alkyl group of carbon numbers 1-8 (meta) - 99.9 weight parts, Are formed by carrying out copolymerization of monomers 0 other than the monomer which has the monomer 0.1 - 20 weight parts which have a functional group, the aforementioned (meta) acrylic ester, and a functional group - the 20 weight parts. The 1st clause [of a claim] written anisotropic conductive adhesives characterized by being the copolymer which has a weight average molecular weight in the polystyrene conversion by GPC analysis within the limits of 100,000-2 million.

[Claim 5] Anisotropic conductive adhesives of either the Claim 1 clause or the 4th clause given in a clause characterized by containing polymerization inhibitor of 0.01 - 50 weight part to a polymerization initiator 100 weight part further in the above-mentioned adhesives component.

[Claim 6] Anisotropic conductive adhesives of either the 1st clause of a claim, or the 4th clause given in a clause with which the above-mentioned adhesives component is further characterized by containing the inorganic particles of 5 - 50 weight part to an acrylic adhesive property component 100 weight part.

[Claim 7] The 1st clause of a claim or anisotropic conductive adhesives given in the 6th clause characterized by for the above-mentioned inorganic particles being in within the limits whose mean particle diameter is 0.05-5.0 micrometers, and having 1/2 or less mean particle diameter of metal content grains.

[Claim 8] The grains by which the metal layer was prepared for the above-mentioned metal content grains in the peripheral face of insulating core material grains, Or they are the grains in which the insulating layer which a metal layer is prepared in the peripheral face of insulating core material grains, and can be removed by heating and/or pressurization on this metal layer surface was formed. Anisotropic conductive adhesives given in the 1st clause of a claim characterized by the mean particle diameter of these metal content grains being 1/2 or less [of the pattern top width by which conductive grains are arranged among the circuit patterns which it is going to paste up].

[Claim 9] The above-mentioned anisotropic conductive adhesives dissolve or distribute an acrylic adhesive property component so that a nonvolatile matter may become 20 to 40weight %. [the coating liquid which made the organic solvent solution or dispersion liquid adjusted to within the limits whose viscosity at 25 degrees C is 50 - 500poise / 25 degrees C distribute metal content grains] Anisotropic conductive adhesives of either the 1st clause of a claim, or an octavus clause given in a clause characterized by having the form of the shape of a tape which applied to the mold releasing film and it was made to dry, or the shape of a sheet.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the anisotropic conductive adhesives for connecting a circuit pattern mutually electrically while pasting up mutually the wiring board with which the circuit pattern was formed in the substrate surface.

[0002]

[Background of the Invention] While making it flow through the circuit pattern which stands face to face against the substrate surface in the wiring boards in which the circuit pattern was formed after the circuit pattern has met, as adhesives to paste up, both substrates for example the adhesives (connection sheet) of the sheet fabricated by thermofusion nature from the adhesives constituent with which conductive grains were distributed in reaction hardening resin like the adhesive component of electric insulation or an epoxy resin are known (JP,S62-206772,A --) Refer to JP,S62-40183,A and JP,S62-40184,A, JP,H5-21094,A, and JP,S60-140790,A.

[0003] If heating pressurization of this connection sheet is carried out in the state where it inserted between two wiring boards While being able to carry out through the conductive grains which it changed [grains] into the state where the insulating adhesive property component shifted to the transverse direction of the overlapping circuit patterns, and only conductive grains were pinched with the circuit pattern, and had the electrical connection of this portion pinched Two wiring boards can be pasted up by the insulating adhesive property component which forms a connection sheet.

[0004] Many thermoplastic adhesives were used as an insulating adhesive property component in the anisotropic conductive adhesives with which the above grains are distributed. By using such thermoplastic adhesive, there is an advantage that it can paste up by carrying out short-time heating pressurization at low temperature comparatively.

[0005] However, there is a field which cannot be referred to as that the anisotropic conductive adhesion using such thermoplastic adhesive has temporal stability with sufficient thermoplastic adhesive which is an

insulating adhesive property component. That is, when it is used on severe conditions -- an adhesive component uses the wiring board pasted up using the anisotropic conductive adhesives which are thermoplastic adhesive by a high-humidity/temperature condition for a long period of time, for example -- an adhesive component plasticizes and it may come to have a flow. And the conductive grains held between circuit patterns may move with a flow of an adhesion component, and the conductivity between circuit patterns, i.e., an electric resistance value, becomes unstable.

[0006] In order to solve such a problem, using a thermosetting resin like an epoxy resin as an insulating adhesive property component is also proposed. If a thermosetting resin is used as an adhesive component, the above moisture-proof thermal stability and reliability can improve sharply, but generally such a thermosetting resin has short working life, and sticking-by-pressure conditions are high temperature, and there is a problem of becoming a long time. For example, it is common to have heated for 20 to 30 seconds and to have pasted up, putting the pressure of 40-50kg/cm² by a 170-180-degree C heat condition, when using the thermosetting adhesive of an epoxy system. If cooking temperature and heat time are short, hardening will be inadequate and sufficient bond strength and flow reliability will not be acquired.

[0007] In the field of the precision electric device for which anisotropic conductive adhesion is needed, the densification of the circuit is achieved and the circuit pattern which carries out anisotropic conductive adhesion is becoming narrowly and thin in recent years. The circuit pattern formed in the substrate which especially consists of a transparent metallic thin film (ITO= indium oxide) of a liquid crystal element, When making it join and flow through TCP (tape carrier package) which carries Driver IC Very narrowly [the adjoining electrode spacing], since wiring is thin, when it pastes up on the conventional anisotropic conductive adhesion conditions, in wiring, exfoliate and also the substrate itself has received [omission and] damage. On the other hand, since an adhesives component softens with change of the service temperature of liquid crystal even if an adhesive component carries out anisotropic conductive adhesion of the circuit pattern of such liquid crystal using the anisotropic conductive adhesives which are thermoplastic adhesive, There is a problem that the electrical property between substrates falls by movement of the conductive grains in adhesives, gap of a substrate, etc.

[0008]

[Objects of the Invention] This inventions are low temperature and low pressure, and aim at offering the anisotropic conductive adhesives which can be pasted up for a short time.

[0009] Furthermore while this inventions are low temperature and low pressure, and being able to harden them by short-time adhesion and being able to make good flow nature discover between good bond strength and the circuit pattern of a different substrate It aims at offering the anisotropic conductive adhesives which can secure this bond strength and flow nature for a long period of time.

[0010]

[Summary of the Invention] The anisotropic conductive adhesives of this invention are anisotropic conductive adhesives which consist of metal content grains distributed in the adhesives component which has insulation, and this adhesives component, and this adhesives component An acrylic adhesive property component, (Meta) by containing the reactant component which has at least two acrylyl groups, and a polymerization initiator this adhesives component hardens by heating or photoirradiation, and is characterized by joining the substrate which is adherend in different direction electric conduction (that is, it arranging so that the circuit pattern formed in the two substrate surface may be confronted each other, and

flow nature being secured between this circuit pattern that confronts each other -- as -- adhesion).

[0011] The anisotropic conductive adhesives of this invention as mentioned above An acrylic adhesive property component, (Meta) Metal content grains are distributed in the adhesives component containing the reactant component and polymerization initiator which have two or more acrylyl groups, and this adhesive component can paste up two substrates which confront each other in different direction electric conduction by heating or photoirradiation while showing insulation.

[0012] And [the component] although the adhesives component which was blended with the anisotropic conductive adhesives of this invention unlike the conventional thermoplastic acrylic adhesives has flowability proper as adhesives before heating or photoirradiation (Meta) By blending the reactant component and polymerization initiator which have two or more acrylyl groups, and performing heating operation or photoirradiation in these adhesives, these acrylic adhesives are hardened and that flowability disappears.

[0013]

[Detailed Description of the Invention] The anisotropic conductive adhesives of this invention are explained concretely hereafter. The anisotropic conductive adhesives of this invention consist of metal content grains distributed in the adhesives component which has insulation, and this adhesives component.

[0014] This adhesives component contains the reactant component which has an acrylic adhesive property component and at least two acrylyl groups (meta), and the polymerization initiator. An acrylic adhesive property component is usually the copolymer of alkyl (meta) acrylate, a functional group content monomer, and other monomers here.

[0015] As an example of the alkyl (meta) acrylate used in this invention Methyl (meta) acrylate, ethyl (meta) acrylate, isopropyl (meta) acrylate, N-butyl (meta) acrylate, isobutyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, iso octyl (meta) acrylate, Lauryl (meta) acrylate, stearyl (meta) acrylate, cyclohexyl (meta) acrylate, etc.; as an example of alkoxy alkyl (meta) acrylate Methoxy ethyl (meta) acrylate, ethoxyethyl (meta) acrylate, etc. can be mentioned. these are independent -- it is -- it can be combined and used. [the acrylic adhesive property component from which using the acrylic ester which especially has the alkyl group of carbon numbers 1-8 by this invention (meta) constitutes the desirable adhesive component of this invention] Copolymerization of the repetition unit guided from the above-mentioned alkyl (meta) acrylate (meta) (acrylic acid alkyl ester) is usually preferably carried out in 78 to 97.5weight % of quantity 60 to 99.9weight %.

[0016] Moreover, as an example of the functional group introduced into the functional group content monomer, a carboxyl group, a hydroxyl group, an amide group, a methylol group, and an epoxy group can be mentioned. As an example of the functional group content monomer into which the above functional groups were introduced Acrylic acid, beta-carboxyethyl acrylate, itaconic acid, (Meta) The monomer containing carboxyl groups, such as crotonic acid, maleic acid, maleic anhydride, and maleic acid butyl, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, The monomer containing hydroxyl groups, such as chloro 2-hydroxypropyl (meta) acrylate, diethylene glycol mono-(meta) acrylate, and allyl alcohol, Aminomethyl (meta) acrylate, dimethylaminoethyl (meta) acrylate, The monomer containing amide groups, such as vinylpyridine, acrylamide (meta), N-methyl (meta) acrylamide, and N-ethyl (meta) acrylamide, The monomer containing epoxy groups containing an amide group and methylol groups, such as N-methylol (metha)acrylamide and dimethylol (meta) acrylamide, such as a monomer and glycidyl (meta) acrylate, etc. can be mentioned. these are independent -- it is -- it can be combined and used. The repetition unit guided from the above-mentioned functional group content monomer is usually carrying out copolymerization to the

copolymer which constitutes the adhesive component of this invention in 2 to 10weight % of quantity preferably zero to 20weight %.

[0017] Furthermore, a styrene system monomer and a vinyl system monomer can be mentioned as other monomers which form an adhesive component by this invention besides the above-mentioned monomer. Specifically as an example of a styrene system monomer Styrene, methyl styrene, dimethyl styrene, bird methyl styrene, Ethyl styrene, diethyl styrene, triethyl styrene, propyl styrene, Alkyl styrene, such as butyl styrene, hexyl styrene, heptyl styrene, and octyl styrene; Flo Ross Tschirren, Halogenation styrene, such as chlorostyrene, bromostyrene, dibromo styrene, and iodine styrene; nitro styrene, acetyl styrene, methoxy styrene, etc. can be mentioned further.

[0018] As an example of a vinyl system monomer, moreover, vinylpyridine, vinyl pyrrolidone, Halogenation vinyl, such as conjugated diene monomer; vinyl chloride, vinyl bromide, etc., such as vinylcarbazole, vinyl acetate, phenyl maleimide and acrylonitrile; butadiene, isoprene, and chloroprene; halogenation vinylidenes, such as vinylidene chloride, etc. can be mentioned.

[0019] these monomers are independent -- it is -- it can be combined and used. Copolymerization of the monomer besides the above can usually be preferably carried out in 0 to 10weight % of quantity zero to 20weight % into the copolymer which constitutes the adhesives of this invention.

[0020] After it supplies the above monomers to a reactional solvent for example, and inert gas, such as nitrogen gas, replaces the air within the system of reaction, heating churning of the acrylic copolymer which constitutes the adhesives component of this invention can be carried out under existence of a reactional initiator as occasion demands, and it can be manufactured by carrying out a polymerization reaction.

[0021] As a reactional solvent used here, it is used by the organic solvent and specifically Aliphatic hydrocarbon, such as aromatic hydrocarbon, such as toluene and xylene, and n-hexane, Ketone, such as fatty alcohol, such as ester species, such as ethyl acetate and butyl acetate, n-propyl alcohol, and iso-propyl alcohol, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone, can be mentioned.

[0022] Moreover, when using a reactional initiator, azobisisobutyronitril, benzoyl peroxide, G tert-butyl peroxide, a cumene hydroperoxide, etc. can be used, for example.

[0023] The reaction temperature of the above-mentioned polymerization reaction is 50-90 degrees C, and reaction time is usually 4 to 12 hours preferably for 2 to 20 hours. Moreover, a reactional solvent is used in the quantity of a 50 - 300 weight part to the total quantity 100 weight part of a monomer. Furthermore, a reactional initiator is usually used in the quantity of 0.01 - 10 weight part.

[0024] the weight average molecular weight in the polystyrene reduced property by GPC analysis of the acrylic adhesion component obtained as mentioned above -- usually -- 100,000-2 million -- it is within the limits of 300,000-1,500,000 preferably.

[0025] Moreover, by polymerizing in a solution as mentioned above usually 50 - 500poise / acrylic adhesive solution which is 50 - 200poise / within the limits of 25 degrees C preferably 25 degrees C is preferably obtained for the viscosity of a solution [in / in nonvolatile matter concentration / 25 degrees C] 20 to 30weight % 20 to 40weight %.

[0026] [in this invention, after removing at least some solvents from such an acrylic adhesive property component solution, can also use it, being able to generate as occasion demands, still more newly being able to add other solvents, and being able to dissolve or distribute acrylic adhesives, but] It is desirable to use the organic solvent solution of the acrylic adhesives obtained by carrying out copolymerization of the

above raw material monomers as it is.

[0027] The acrylic adhesive property component obtained as mentioned above is thermoplasticity, is ordinary temperature, and has adhesion nature. The adhesives component which shows the insulation used by this invention contains the reactant component which has the above acrylic adhesive property components and at least two acrylyl groups (meta), and the polymerization initiator.

[0028] The number of repetitions of unit structure (degree of polymerization) is about two to 20 polymer, the general concept of the oligomer and the prepolymer which are used by this invention is not enough as a degree of polymerization, and a high molecular compound is a polymerization thing of one step of polymer (high molecular compound) this side which has not become.

[0029] As a reactant component which has at least two acrylyl groups (meta) here, the oligomer or the prepolymer which has the polyfunctional monomer which has two or more acrylyl groups (meta), and two or more acrylyl groups (meta) can be mentioned.

[0030] As an example of the polyfunctional monomer which has two or more acrylyl groups (meta) here Ethylene glycol di(metha)acrylate, neopentyl glycol diacrylate, 1,6-hexanediol di(metha)acrylate, trimethylolpropane triacrylate, pentaerythritol bird acrylate, etc. can be mentioned.

[0031] moreover, as an example of the oligomer which has two or more acrylyl groups (meta), and a prepolymer Pori ethylene-glycol-di(metha)acrylate, pentaerythritol bird acryloyl hexamethylene diisocyanate, and bisphenol A-diepoxy (meta) acrylate etc. can be mentioned.

[0032] these are independent -- it is -- it can be combined and used. [the reactant component which has such (meta) at least two acrylyl groups] It follows on the polymerization initiator contained in the adhesives component in this invention being activated like the usual radical polymerization reaction. The initiator radical which the activated initiator cleft and generated induces cleavage and chain reaction of an ethylene nature unsaturation component, and a reactant component forms polymer-ized network structure or polymer IPN structure.

[0033] the reactant component which has at least two above (meta) acrylyl groups receives an acrylic adhesive property component 100 weight part -- usually -- a 1 - 100 weight part -- desirable -- 5 - 50 weight part -- it is especially used in the quantity of 10 - 40 weight part preferably. By blending the reactant component which has at least two acrylyl groups (meta) in the above quantity The adhesive component of this invention is activated by the polymerization initiator mentioned later, polymer network structure or polymer IPN structure is formed, and the adhesive component of this invention is hardened and stops showing thermoplasticity with formation of such the structure of cross linkage. Furthermore, when the reactant component which has at least two acrylyl groups (meta) in the above quantity is blended, before hardening, the reactant component which has these (meta) at least two acrylyl groups acts as a plasticizer, and this adhesive component comes to have good flowability.

[0034] In this invention, the polymerization initiator contains further for the adhesive component. A thermal polymerization initiator and/or a photopolymerization initiator can be used as a polymerization initiator by this invention.

[0035] As a thermal polymerization initiator used by this invention, organic peroxide, an inorganic peroxide, an azo thermal polymerization initiator, etc. can be mentioned. As an example of the thermal polymerization initiator of an organic peroxide system, benzoyl peroxide, lauroyl peroxide, octanoyl peroxide and 3 and 5, and 5-trimethylhexanoyl peroxide can be mentioned here.

[0036] Moreover, potassium persulfate and ammonium persulfate can be mentioned as an example of the thermal polymerization initiator of an inorganic peroxide system. Furthermore, as an example of an azo thermal polymerization initiator, azobisisobutyronitrile, 2, and 2'-azobis 2-methyl butyronitrile and 4, and 4-azobis 4-SHIANOBARERIKKUASHIDDO can be mentioned.

[0037] the above thermal polymerization initiators are independent -- it is -- short-time hardening can be enabled by selecting suitably with the cooking temperature at the time of being able to combine and use it and joining.

[0038] Moreover, in this invention, a photopolymerization initiator can also be used with the thermal polymerization initiator instead of the above thermal polymerization initiators. In this invention, a carbonyl compound, a sulfur compound, and an azo compound can be used as a photopolymerization initiator.

[0039] As an example of a photopolymerization initiator, acetophenone, benzophenone, benzyl benzoin, benzoin ether, azo-isobutyro-dinitrile, benzoyl peroxide, and JITASARU butyl peroxide can be mentioned here.

[0040] After the polymer network structure or polymer IPN structure by the reactant component which has at least two acrylyl groups (meta) mentioned above in the adhesive component by blending such a polymerization initiator is formed and such structure is formed, the characteristics of plasticizing if it heats disappear.

[0041] as opposed to the reactant component 100 weight part in which the above polymerization initiators have at least two acrylyl groups (meta) -- usually -- 0.1 - 10 weight part -- it is preferably blended in the quantity of 1 - 7 weight part. Since polymer network structure or polymer IPN structure is formed of the reactant component which has at least two above-mentioned acrylyl groups (meta) by blending a polymerization initiator in the above quantity and a cured body is formed of it, it is lost that this adhesion component shows flowability after adhesion. Therefore, even if the substrate pasted up using the anisotropic conductive adhesives of this invention is the case where it is used under a high-humidity/temperature condition, it becomes difficult to change the bond strength and the electrical property of this substrate.

[0042] Furthermore, the cross linking agent may contain for the above-mentioned adhesive component. This cross linking agent is the compound which can form the structure of cross linkage, even if a polymerization initiator does not exist unlike the reactant component which has at least two above-mentioned acrylyl groups (meta).

[0043] as the example of such a cross linking agent -- N, N, N', and N' - tetraglycidyl ether meta-xylene diamine and tolylene diisocyanate trimethylol propane -- Hexamethylene di-isocyanate and screw iso phthaloyl 1- (2-methylaziridine) and tetramethylolmethane tree beta-aziridinyl propionate can be mentioned.

[0044] such a cross linking agent receives an acrylic adhesive property component 100 weight part -- usually -- 0 - 10 weight part -- it is preferably blended in the quantity of 0 - 1 weight part. Furthermore, it is desirable to blend quinone or polymerization inhibitor like nitroaromatic into the adhesive component used by this invention, in order to inhibit the polymerization reaction by the reaction of the above-mentioned polymerization initiator, for example at the time of preservation and conveyance etc.

[0045] Hydroquinone and methyl ether hydroquinone can be mentioned as an example of polymerization inhibitor here. thus -- in using polymerization inhibitor, polymerization inhibitor receives a polymerization initiator 100 weight part -- usually -- 0.01 - 50 weight part -- desirable -- 1 - 50 weight part -- it is especially blended in the quantity of 5 - 30 weight part preferably. While the time of preservation and a transfer etc. can

control advance of the polymerization reaction under the situation where it is not planning, by blending polymerization inhibitor in the above quantity The reactivity of the reactant component which has at least two acrylyl groups (meta) at the time of heating sticking by pressure or photoirradiation sticking by pressure is not spoiled.

[0046] Furthermore, it is desirable to blend various coupling agents like a silane coupling agent with the adhesive component which has the insulation used by this invention, for example. this coupling agent receives an acrylic adhesive property component 100 weight part -- usually -- 0.5 - 3 weight part -- it is preferably blended in the quantity of 1 - 2 weight part.

[0047] Metal content grains are distributed in the adhesive component which the anisotropic conductive adhesives of this invention become from the above components. The pre-insulation metal grains from which the surface of metal grains and metal grains was covered with the insulating component by the metal content grains used by this invention, A metal layer is formed in the surface of the metallic-coating grains by which the metal layer was formed in the surface of an insulating core material, and an insulating core material, and there are pre-insulation grains by which this metal layer was further covered with the insulating component.

[0048] As metal grains used here, pewter, Zn, aluminum, Sb, U, Cd, Ga, Ca, Au, Ag, Co, Sn, Se, Fe, Cu, Th, Pb, nickel, Pd, Be, Mg, Mn, etc. are used. These metals may be used independently, or may use two or more sorts, and may add other elements, a compound, etc. further for modification, such as hardness and surface tension.

[0049] Moreover, pre-insulation metal grains are grains covered with the insulating component for which the surface of the above metal grains can expose the metal grain surface by pressurization in the case of adhesion (it heats further). Such an insulating layer can be formed with resin, a wax, non-subtlety fine particles, etc. It is desirable especially to form by this invention with non-subtlety fine particles, such as resin, such as a fluororesin, an acrylate resin (meta), a styrene resin, Kalna Barrow, polypropylene, or polyethylene, or silica.

[0050] Metallic-coating grains are grains by which the conductive metal layer was formed in the surface of an insulating core material. As an insulating core material, specifically here Polyethylene, polypropylene, Polystyrene, a methyl methacrylate styrene copolymer, an acrylonitrile styrene copolymer, Acrylonitrile Butadiene Styrene, polycarbonate, Various acrylate, such as polymethylmethacrylate, and polyvinyl butyral, Polyvinyl formal, polyimide, polyamide, polyester, polyvinyl chloride, Polyvinylidene chloride, a fluororesin, polyphenylene oxide, a polyphenylene ape fight, Pori methyl pentene, a urea resin, a melamine resin, benzoguanamine resin, Phenol formalin resin, a phenol resin, xylene resin, furan resin, diallyl phthalate resin, an epoxy resin, polyisocyanate resin, phenoxy resin, silicone resin, etc. can be mentioned. Polystyrene, polymethylmethacrylate, a methyl methacrylate styrene copolymer, a phenol resin, and silicone resin are [among these] especially desirable. These resin can also be used independently, and two or more sorts can also be mixed and used for it. Furthermore, these resin may denaturalize suitably. Moreover, by adding and making additives, such as a cross linking agent and a curing agent, react if needed, the structure of cross linkage may be formed and you may be a cured body further.

[0051] Although a core material is manufactured by making such a resin material granular conventionally using a well-known method, it is desirable that the grain size is uniform. As the manufacture method of such a core material, specifically An emulsion-polymerization method, a soap free emulsion-polymerization

method, a seed emulsion-polymerization method, a suspension-polymerization method, the nonaqueous dispersion polymerizing method, a dispersion polymerization method, an interfacial-polymerization method, the in-situ polymerizing method, hardening-among liquid coating, the dry technique in liquid, a fusion dispersion cooling method, the spray-drying method, etc. can be illustrated.

[0052] The metal layer which consists of metals, such as pewter, Zn, aluminum, Sb, U, Cd, Ga, Ca, Au, Ag, Co, Sn, Se, Fe, Cu, Th, Pb, nickel, Pd, Be, Mg, and Mn, is formed in the above core material surfaces.

[0053] As a method of forming a metal layer on the surface of a core material using such a metal For example, vacuum deposition, the sputtering method, the ion plating method, the plating method, The chemical process which carries out the chemical bond of the metal to the core material surface which physical methods, such as a spraying process, can be used, and also consists of resin which has a functional group through a coupling agent etc. if needed, When compounding the method of making a metal sticking to the core material surface using a surface active agent etc., and resin which is the material of a core material, metal powder can be distributed in a monomer, and the method of making metal powder sticking to the surface of the core material 7 made of resin after a polymerization etc. can be mentioned.

[0054] Thus, as for the formed metal layer, it is desirable to be attached so that modification of a core material may be followed and it may transform, when heating pressurization is carried out grains.

Furthermore, this metal layer does not need to be a lamina and two or more layers may be laminated.

[0055] Pre-insulation grains are grains which covered further with the insulating component the surface of the grains by which the metal layer was formed as mentioned above in the core material surface so that the metal layer surface might be exposed with the pressurization in the case of adhesion (it heats further). Such an insulating layer can be formed with resin or a wax, non-subtlety fine particles, etc. like the above. It is desirable especially to form by this invention with non-subtlety fine particles, such as resin, such as a fluororesin, an acrylate resin, a styrene resin, Kalna Barrow, polypropylene, or polyethylene, and silica.

[0056] Such an insulating layer can be formed using well-known methods, such as the method of immersing into the solution containing the resin which forms an insulating layer for metallic-coating grains. It is desirable to form this insulating layer by the dry blending method which mixes the insulating component of the shape of a particle of especially the above to metallic-coating grains, without minding a liquid, and forms an insulating layer in this invention by applying compressive force, shearing force, impulse force, etc. further if needed.

[0057] The particle diameter of the metal content grains used by this invention is made smaller than the interval of the circuit pattern which carries out different direction electric conduction adhesion. Usually, as for the particle diameter of this metal content grain, usual has 1-50 micrometers of mean particle diameter [2-20 micrometers of] of 2-10 micrometers still more preferably preferably.

[0058] Moreover, in the case of metallic-coating grains, the average thickness of a metal layer has preferably usual [0.01-10.0 micrometers of / 0.05-5 micrometers of] within the limits of 0.2-2 micrometers still more preferably. Moreover, as for the metal layer, the ratio of the diameter of metal layer thickness / core material usually has $1 / 100 - 1/5$, and the thickness that becomes within the limits of $1 / 50 - 1/10$ preferably.

[0059] furthermore, the average thickness of the insulating layer in pre-insulation grains -- usually -- there are 0.1-2 micrometers within the limits of 0.2-1 micrometer still more preferably preferably, and 0.01-5 micrometers receives the mean particle diameter of a core material -- usually -- $1 / 50 - 1/5$ -- it has the

thickness of $1/20 - 1/10$ preferably.

[0060] the width of the top of the circuit pattern with which conductive grains are arranged among the circuit patterns in which the mean particle diameter of the metal content grains furthermore used by this invention usually tends to carry out anisotropic conductive adhesion -- it has $1/3$ or less mean particle diameter preferably $1/2$ or less. That of the top of a circuit pattern means the width of the top end of the circuit pattern currently formed by being close on the substrate here, and the width of the circuit pattern part of a substrate and the stuck portion is called bottom width. In the circuit pattern to which conductive adhesion is performed, the direction of the top end of a circuit pattern, i.e., top width, is narrower than bottom width on the process which forms this circuit pattern. That is, when the mean particle diameter of conductive grains is larger than one half of the top width of a circuit pattern, conductive grains fall between circuits from on a circuit, and good flow nature may not be obtained, and when conductive grains are still larger, it may short-circuit between circuits. Moreover, when the mean particle diameter of conductive grains is smaller than $1/10$ of the top width of a circuit pattern, the point of contact of conductive grains and a circuit pattern becomes small, and good flow nature is not obtained.

[0061] as opposed to the adhesive component 100 weight part in which the above metal content grains have insulation in the anisotropic conductive adhesives of this invention -- usually -- 1 - 50 weight part -- it is preferably blended in the quantity of 5 - 20 weight part. While good flow nature is securable between substrates by blending metal content grains in such a quantity, there is also no fall of the bond strength between the substrates accompanying having blended metal content grains.

[0062] Although the anisotropic conductive adhesives of this invention consist of an adhesion component which has insulation as mentioned above, and metal content grains distributed in this adhesion component and it has outstanding characteristics By blending with these anisotropic conductive adhesives the inorganic particles which have further specific particle diameter, a flow of resin in the constituent at the time of adhesion (adhesion component) can be controlled.

[0063] That is, inorganic particles can be further blended with the anisotropic conductive adhesives of this invention. As inorganic particles which can be used here, mean particle diameter usually uses 0.01-5.0 micrometers of 0.02-1.0-micrometer insulating inorganic powder preferably. Furthermore, as for this inorganic particle, usual [of metal content grains] has the mean particle diameter of $1/10 - 1/100$ preferably $1/2$ or less. Moreover, it is usable, even if particle diameter is the thing of simple distribution and it is the thing of double distribution as such inorganic particles.

[0064] As a concrete example of such inorganic particles, titanium oxide fine-particles grains, silicon dioxide fine-particles grains, calcium carbonate fine-particles grains, calcium phosphate fine-particles grains, aluminium oxide fine-particles grains, antimony trioxide fine-particles grains, etc. can be mentioned. Such inorganic particles are independent, or can be combined and used.

[0065] as opposed to the adhesive component 100 weight part to which the above inorganic particles have insulation in the constituent of this invention -- usually -- a 1.0 - 50.0 weight part -- it is preferably blended in a quantity of a 3.0 - 25.0 weight part within the limits.

[0066] In the anisotropic conductive adhesives of this invention, especially a fluid state can use the rate of a compounding ratio of an adhesives component and inorganic particles as the constituent adjusted suitably by carrying out within the limits of 100:1-10:1 by a bulk density.

[0067] Thus, by blending inorganic particles, the flowability of the anisotropic conductive adhesives of this

invention in the case of heating pressurization adhesion can be adjusted. And a flow of the adhesives at the time of high temperature and movement of the electric conduction filler accompanying it, and defective continuity are lost by blending the above inorganic particles.

[0068] Although the anisotropic conductive adhesives of this invention contain the inorganic particles blended by the adhesives component, the metal content grains, and necessity of having insulation as mentioned above, other components may be further blended within limits which do not spoil the characteristics of the anisotropic conductive adhesives of this invention.

[0069] For the adhesive component which has insulation, for example, a phenol resin, a urea resin, A silane coupling agent like thermosetting resins, such as a melamine resin and benzoguanamine resin, and an epoxy silane system coupling agent, An isocyanate system curing agent, an epoxy system curing agent, a metal chelating agent system curing agent and curing agents, such as a melamine system curing agent, a weathering agent, a heat-resistant stabilizer, a color, a pigment, etc. can be blended.

[0070] Furthermore, in an adhesives component, what is called a tackifier (tackifier) can also be added as an adhesion modifier. As an example of the tackifier which can be used here, cumarone indene resin, alkyl FANORU resin, denaturation xylene resin, terpene resin, a rosin modified resin, etc. can be mentioned. receiving an acrylic adhesive property component 100 weight part, when using such a tackifier -- usually -- a 0.01 - 100 weight part -- it is 5 - 50 weight part preferably.

[0071] Although different direction electric conduction adhesion can be carried out by [which applied the anisotropic conductive adhesives of this invention to the adhesion schedule side of a substrate, for example with which pasty form, and removed the solvent] irradiating electron rays, such as ultraviolet radiation, being afterbaking-stuck by pressure or pressurizing After applying the anisotropic conductive adhesives of this invention on a releasing paper etc., a solvent is removed, and it can also be used for it, carrying out size enlargement to the shape of a tape, or the shape of a sheet. [for example, the organic solvent solution or dispersion liquid whose viscosity at 25 degrees C which dissolves or distributed the acrylic adhesive property component as mentioned above so that a nonvolatile matter might become 20 to 40weight % is 50 - 500poise / 25 degrees C] It can be used for the form of the shape of a tape, or the shape of a sheet by distributing above-mentioned metal content grains, preparing coating liquid, and making it dry, after applying this coating liquid to the base material superiors which have detachability, carrying out.

[0072] For example, anisotropic conductive adhesion which uses the anisotropic conductive adhesives of this invention by which size enlargement was carried out to the shape of a tape is performed as follows. As shown in drawing 1 , first, while was formed, and an electrode 2 lays the anisotropic conductive adhesives 4 of the shape of a tape which has a releasing paper 5 on the upper surface in the adhesion schedule part 3 of the end of a substrate 1, presses down lightly for 2 to 9 seconds the temperature of 20-40 degrees C, and time, and carries out temporary adhesion of the anisotropic conductive tape-like adhesives 4 on a substrate. Subsequently, a releasing paper is removed, from on the anisotropic conductive adhesives 4 by which temporary adhesion was carried out, another substrate 6 with which the electrode 12 was formed is piled up, and alignment is performed. Subsequently, it pressurizes, while heating jointing by which alignment was carried out as mentioned above, and actual adhesion of a substrate 1 and the substrate 6 is carried out.

[0073] [the cooking temperature in the case of this adhesion at the time of using the anisotropic conductive adhesives of this invention] Usually, by 120-160 degrees C, the pressure to give is 10-30kg/cm², heating press time is 5 to 10 seconds, rather than the case where the conventional anisotropic conductive adhesives

are used, cooking temperature can be set up low and heating press time is also shortened further.

[0074] The circuit patterns 2 and 12 are electrically connected by the metal content grains 10 between two substrates pasted up as mentioned above. Furthermore, by carrying out heating pressurization, flowing so that between substrates 1 and 6 may be filled, in the stage in early stages of heating, the adhesives component which has flowability is hardened gradually and pastes up a substrate 1 and a substrate 6 mutually.

[0075] Moreover, when the anisotropic conductive adhesives of this invention contain a photopolymerization initiator, in the above-mentioned method, different direction electric conduction adhesion can be carried out by irradiating energy lines, such as ultraviolet radiation, from the glass substrate side instead of heating.

[0076] By performing anisotropic conductive adhesion as mentioned above using the anisotropic conductive adhesives of this invention, as shown in drawing 2, between the circuit patterns 2 and 12 which confront each other, the metal content grains 13 are pinched and between the circuit pattern 2 and 12 is electrically connected by this metal content grain. On the other hand, the substrate portion in which the circuit patterns 2 and 12 are not formed is firmly pasted up by the cured body of the adhesion component which has insulation.

[0077] And this adhesive component hardens the anisotropic conductive adhesives of this invention heating the adhesive component which had flowability at the beginning, or by carrying out photoirradiation, and flowability disappears. Therefore, even if it exposes the substrate pasted up using the anisotropic conductive adhesives of this invention to conditions severe for a long period of time, bond properties, electrical properties, etc., such as bond strength, are not changed easily.

[0078] Moreover, different direction electric conduction adhesion can be performed good, without doing damage to urgency these days also to the circuit pattern with which fine pitch-ization is progressing in the case of sticking by pressure, since it can paste up on conditions milder than the conventional anisotropic conductive adhesives. Furthermore, since cooking temperature is also low, also when pasting up a flexible-printed-wiring board, a wiring board for liquid crystal elements, etc. with which the circuit pattern was formed on a film-like board, it is rare [it / sticking-by-pressure time is short, and] to do damage to these substrates.

[0079] In addition, when the grains which have an insulating layer are used for the surface as metal content grains, with a pressure (it heats further), it is removed from the grain surface, a metal side is exposed, and good conductivity discovers the insulating layer of the metal content grains pinched with the circuit pattern.

[0080]

[Effect of the Invention] The anisotropic conductive adhesives of this invention consist of metal content grains distributed in the adhesives component which has insulation, and this adhesive component, and this adhesives component An acrylic adhesive property component, (Meta) Since the reactant component which has at least two acrylyl groups, and the polymerization initiator are contained, moreover, different direction electric conduction adhesion of the substrate can be carried out on mild conditions in a short time. And the anisotropic conductive adhesives of this invention have flowability, before performing heating or photoirradiation, but they form a cured body by heating or photoirradiation. Therefore, even if it uses the substrate pasted up with the anisotropic conductive adhesives of this invention at the place where temperature is high, or a humid place, the bond performance does not fall, therefore the electrical property between substrates is not changed.

[0081] Moreover, the time which adhesion takes by using the anisotropic conductive adhesives of this

invention differs from the conventional anisotropic conductive adhesives. In order to be based on the rapid cure reaction by radical development, when ending for a short time and heating moreover, cooking temperature can also be pasted up at low temperature rather than the case where the conventional anisotropic conductive adhesives are used. Therefore, while it decreases remarkably that electronic parts cause heat deterioration with heating in the case of adhesion etc., even when pasting up a heat-resistant low wiring board comparatively, for example like a flexible-printed-wiring board or the wiring board for liquid crystal, it is hard to generate exfoliation of a circuit pattern etc.

[0082] Furthermore, since the anisotropic conductive adhesives of this invention can form a cured body heating or by carrying out photoirradiation within low temperature, low pressure, and a short time, Even if it pastes up the substrate with which the highly minute circuit (fine pitch pattern) to which it is going quickly in recent years was formed The poor circuit or poor flow nature accompanying the adhesives which anchor to polyimide or a polyester film softening a copper foil circuit, and a circuit shifting or receiving desorption and damage etc. does not occur.

[0083]

[Working example] Although a work example explains this invention below, this invention is not limited to these work examples.

[0084]

[A work example 1] The acrylic adhesives (A) of the presentation shown below according to a conventional method were prepared.

Ethyl acrylate 50 weight part butyl acrylate 42 weight part acrylic acid Three weight part acrylic acid 2-hydroxyethyl The 5 weight part above-mentioned reaction was performed by using toluene and an ethyl acetate mixed solvent as a reactional solvent, and using azobisisobutyronitrile as a polymerization initiator.

[0085] The nonvolatile matter of toluene of the obtained acrylic adhesives (A) and an ethyl acetate mixed solution was 30 weight %, and the viscosity at 25 degrees C of this solution was 180poise / 25 degrees C. Moreover, the weight average molecular weight in the styrene reduced property by GPC of the obtained acrylic adhesives (A) was 500,000.

[0086] Independently, the 0.2-micrometer-thick nickel layer was formed in the surface of a polystyrene grain with a mean particle diameter of 10 micrometers, the 0.1-micrometer-thick gold layer was further formed on it, and conductive grains were prepared.

[0087] Acrylic adhesives (A), 3 organic-functions compounds, a thermal polymerization initiator, silica powder, conductive grains, N, N, N', and N' - tetraglycidyl ether meta-xylene diamine and a silane coupling agent were blended in the following quantity, the anisotropic conductive constituent was prepared, this was applied on the releasing paper by a thickness of 15 micrometers, and the anisotropic conductive adhesive film was manufactured.

[0088]

Acrylic adhesives (A) 100 Weight Part Trimethylolpropane Triacrylate 10 Weight Part BENSOIRU Peroxide 0.1 Weight Part Silica Powder 10 Weight Part Conductive Grains 15 Weight Part N, N, N', and N' - Tetraglycidyl Ether Meta-Xylene Diamine 0.02 Weight Part [Silane Coupling Agent] 5 Using Sticking-by-Pressure Condition: Sticking-by-Pressure Head (1.5Mm Width X50Mm) Using Anisotropic Conductive Adhesive Film Which is Weight Part above, and was Made and Manufactured [Heating Sticking-by-

Pressure Conditions for 130 Degree-CX20 Kgf/cm²X 10 Seconds] TCP (top 25 micrometers in width of a 70-micrometer pitch circuit and a copper foil circuit, bottom 30 micrometers in width, 40 micrometers of space parts, 300 pins), and a liquid crystal substrate (glass / ITO solid board, =) Heating sticking by pressure of 8ohms / the ** article was carried out.

[0089] The conduction resistance value between 2 pins of the TCP circuit pasted up as mentioned above is measured, and it is shown in Table 1 by making a result into flow reliability. Moreover, in the inside "-25.85-degree-C cycle" of Table 1, based on the method specified to JIS-C-7021-1977, the resistance at the time of 500 cycle ***** is shown.

[0090] Furthermore, it is shown in Table 1 by making into adhesion reliability the result of having measured bond strength according to JIS-Z-0237. In addition, after carrying out heating sticking by pressure on condition of the above with an "initial value" in Table 1, It is 23 degrees C and the value after neglecting it on condition of RH 65% for 2 hours, "high-humidity/temperature examinations" is 80 degrees C and the value after neglecting it in RH 90% for 500 hours, and "high-temperature testing" is the value after neglecting it at 100 degrees C for 500 hours.

[0091]

[A comparative example 1] In the work example 1, anisotropic conductive adhesives were similarly manufactured except having changed the presentation as follows.

[0092]

Acrylic adhesives (A) 100 Weight Part Silica Powder 10 Weight Part Conductive Grains 12 Weight Part N, N', and N' - Tetraglycidyl Ether Meta-Xylene Diamine 0.02 Weight Part [Silane Coupling Agent] 5 Adhesion reliability and flow reliability are shown in Table 1 about the anisotropic conductive adhesives of the weight part above.

[0093]

[A comparative example 2] In the work example 1, anisotropic conductive adhesives were similarly manufactured except having changed the presentation as follows.

[0094]

Acrylic adhesives (A) 100 Weight Part Epoxy Resin (Ciba-Geigy Japan Make, 100% of Nonvolatile Matter 100 Weight Part Epicure 3010(Product made from Oil Recovery Shell Epoxy)) 2.5 Weight Part Silica Powder 35 Weight Part Conductive Grains 30 Weight part Silane coupling agent 5 Adhesion reliability and flow reliability are shown in Table 1 about the anisotropic conductive adhesives of the weight part above.

[0095]

[A work example 2] Acrylic adhesives (A), 3 organic-functions compounds, a photopolymerization initiator, silica powder, Conductive grain, 4, and 4-bis(diethylamino) benzophenone and a silane coupling agent were blended in the following quantity, the anisotropic conductive constituent was prepared, this was applied on the releasing paper by a thickness of 15 micrometers, and the anisotropic conductive adhesive film was manufactured.

[0096]

Acrylic adhesives (A) 100 Weight Part Trimethylolpropane Triacrylate 10 Weight Part Benzoin Ethyl Ether 0.5 Weight Part 4 and 4-Bis(Diethylamino) Benzophenone 0.2 Weight Part Silica Powder 10 Weight Part Conductive Grains 15 Weight Part Silane Coupling Agent 5 Use Anisotropic Conductive Adhesive Film Which is Weight Part above, and was Made and Manufactured. The high-pressure mercury lamp was

irradiated for 10 seconds from the glass substrate side, having heated beforehand the sticking-by-pressure head (1.5mm width x50mm) at 90 degrees C, and sticking TCP (a 70-micrometer pitch circuit, 300 pins) and a liquid crystal substrate (glass / ITO solid board, 8ohms / ** article) by pressure by the pressure of 20 kgf/cm2.

[0097] The wavelength of this high-pressure mercury lamp was 3000-4000A, and exposure gross energy was 1600mW-sec/cm2. The adhesion reliability and flow reliability between 2 pins of the TCP circuit pasted up as mentioned above are shown in Table 1.

[0098]

[Table 1]

表 1

	接着信頼性			導通信頼性（抵抗値）					
	接着力		耐定荷重試験 80℃, 11.25g/1.5mm	高温高湿試験		高温試験		-25℃・85℃ 500% 100%	
	初期 (gf/cm)	高温高湿 (gf/cm)		初期 (Ω)	500hr (Ω)	初期 (Ω)	500hr (Ω)		
実施例 1	1200	1500	24hr後Ab* vなし	1.8	2.5	1.8	2.2	1.8	2.2
比較例 1	950	1200	24hr以内に落下	2.0	1000以上	2.0	500以上	2.0	1000以上
比較例 2	100	1100	30分以内に落下	10	1000以上	10	1000以上	10	1000以上
実施例 2	1000	1400	24hr後Ab* vなし	2.0	2.8	2.1	2.5	2.0	2.4

[Translation done.]